

# Wet-Chemical Etching of Silicon

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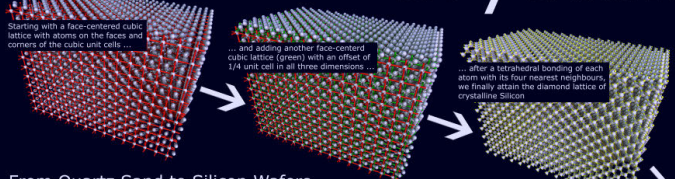
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## Our Poster „Crystalline Silicon“

Crystallography, etch rates of Si (isotropic and anisotropic) and  $\text{SiO}_2$ , Si-wafer production, summarized on a DIN A0 Poster ... Interested? Gladly we send you one or more posters for free (only valid for Europe)! Just send us a short e-mail: [info@microchemicals.de](mailto:info@microchemicals.de)

### Some Crystallography



### From Quartz Sand to Silicon Wafers

The visible matter of the universe is dominated by hydrogen and helium, and the mass fraction of Silicon is less than 0.1 %.

The entire terrestrial globe contains approx. 17 % Silicon. In the approx. 40 km thick earth crust, Silicon (in form of silicates and  $\text{SiO}_2$ ) with a mass fraction of 26 % is the second most element after oxygen.

Quartz sand ( $\text{SiO}_2$ ) is reduced with carbon in an electric arc furnace at > 1900°C to metallurgical-grade Silicon (> 99.999999 %). After thermal decomposition of the HSiCl<sub>3</sub> to polycrystalline Silicon, monocrystalline Silicon is formed via two alternative techniques ...

The metallurgical-grade Silicon is converted into trichlorosilane gas ( $\text{HSiCl}_3$ ) using hydrochloric acid. Multiple distillation of  $\text{HSiCl}_3$  improves the purity up to 99.9999999999 %. After thermal decomposition of the HSiCl<sub>3</sub> to polycrystalline Silicon, monocrystalline Silicon is formed via two alternative techniques ...

**Czochralski-Process**  
A small monocrystalline seed crystal is pulled from a melt of polycrystalline silicon in a quartz carbon crucible. The pull velocity (some mm ... cm per hour) determines the crystal diameter. Advantages: Big crystal diameters, comparable low-cost technique. Disadvantages: Impurities from the crucible, inhomogeneous doping.

**Zone Melting**  
A monocrystalline seed crystal is brought into contact with a polycrystalline Si ingot. Starting from here, an RF coil melts the poly-Si which, after cooling down, forms monocrystalline Si with the crystallographic orientation of the seed crystal. Advantages: No impurities from the crucible, homogeneous doping. Disadvantages: High cost process, limited crystal diameter.

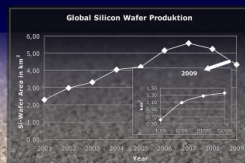
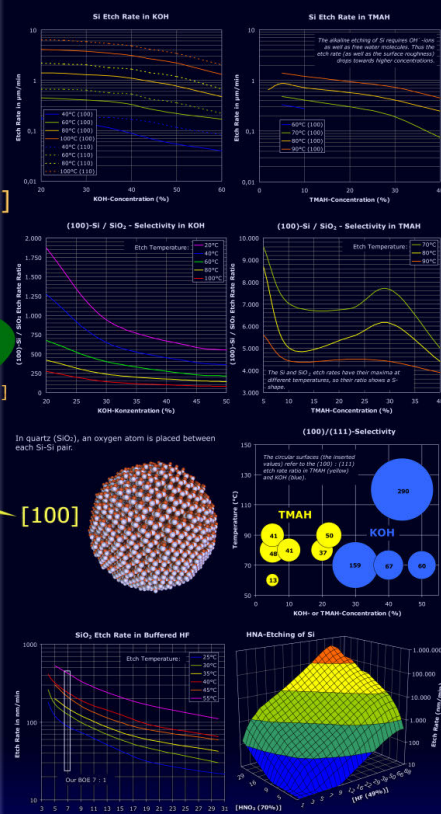
The ingot is cut and ground to the required length and diameter. An orientation flat is added to indicate the crystal orientation. The edge of the sliced wafers is etched to remove the damaged surface resulting from the previous lapping. Finally, it is polished to a mirror surface by a combined mechanical-chemical action, and cleaned.

# Crystalline Silicon

### Silicon Characteristics

Density: 2.33 (quartz: 2.65) g/cm<sup>3</sup>  
Mohs hardness: 6.5 (Ti: 6, quartz: 7, diamond: 10)  
Melting point: 1410 (quartz: 1713) °C  
Boiling point: 2355 °C  
Melting heat: 52.2 (Al<sub>2</sub>O<sub>3</sub>: 6, Al: 10.7) kJ/mol  
Evaporation heat: 384 (H<sub>2</sub>O: 44, Al: 293) kJ/mol  
Specific heat: 0.70 (H<sub>2</sub>O: 4.18, Al: 0.90) J/g K  
Thermal conductivity: 150 (Cu: 400, stainless: 20-50) W/m-K  
Therm. expan. coeff.: 2 (quartz: 0.5, Al: 23) 10<sup>-6</sup>/K

### Wet Chemical Etching of Silicon and $\text{SiO}_2$



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- Si-wafers and yellow light/oils
- Photoresists, developers, removers, adhesion promoters
- YLSI and ULSI solvents and etchants

MicroChemicals GmbH  
Schillerstraße 13, 89077 Ulm, Germany  
[info@microchemicals.eu](mailto:info@microchemicals.eu) [www.microchemicals.eu](http://www.microchemicals.eu)

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## Our Si Wafer Stock List: Si-Wafers.

Since 2010, we supply our customers - beside photoresists, solvents, and etchants - also with c-Si wafers (2 - 8 inch, one- and double-side polished, optionally with  $\text{SiO}_2$  and  $\text{Ni}_3\text{N}_4$ ). Therefore, we are happy to provide you with technical support also in this field of microstructuring. Thank you for your interest!

**Photoresists, developers, remover, etchants, solvents and Silicon wafers ...**

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## Anisotropic Silicon Etching

Strong alkaline substances (pH > 12) such as aqueous KOH- or TMAH-solutions etch Si via  $\text{Si} + 4 \text{OH}^- \rightarrow \text{Si(OH)}_4 + 4\text{e}^-$ .

Since the bonding energy of Si atoms is different for each crystal plane, and KOH/TMAH Si etching is not diffusion- but etch rate limited, Si etching is highly anisotropic: While the {100}- and {110}-crystal planes are being etched, the stable {111} planes act as an etch stop:

**{111}-orientated** Si-wafers are almost not attacked by the etch.

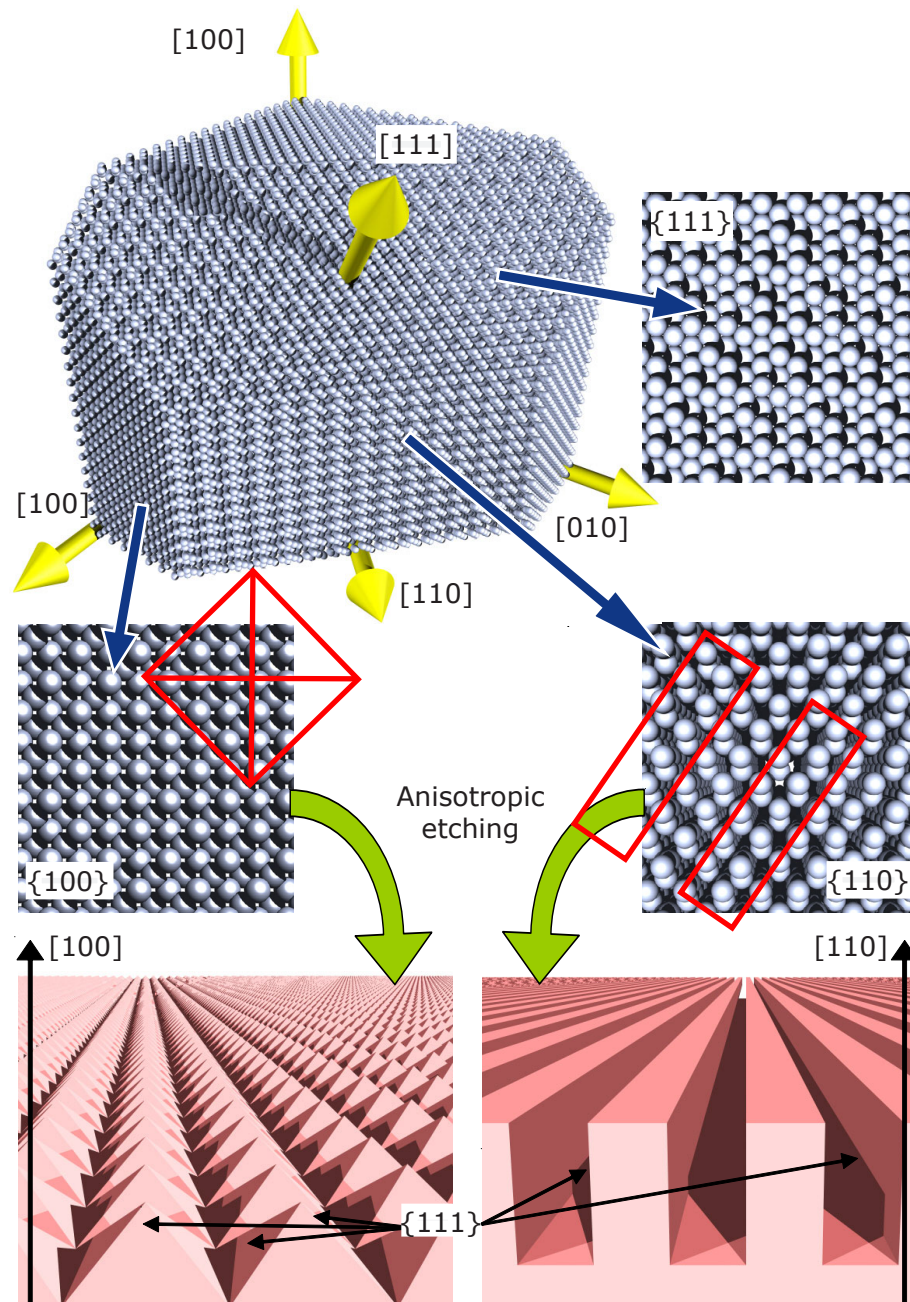
**{100}**-orientated wafers form square-based pyramids with {111} surfaces. These pyramids are realised on c-Si solar cells for the purpose of reflection minimization.

**{110}**-orientated wafers form perpendicular trenches with {111} side-walls, used as e. g. microchannels in micromechanics and microfluidics.

The degree of anisotropy (= etch rate selectivity between different crystal planes), the etch rates, and the etching homogeneity depend on the etching temperature, atomic defects in the silicon crystal, intrinsic impurities of the Si crystal, impurities (metal ions) by the etchant, and the concentration of Si-atoms already etched.

The doping concentration of the Si to be etched also strongly impacts on the etching: During etching, Boron doped Si forms borosilicate glass on the surface which acts as etch stop if the boron doping concentration exceeds  $10^{19} \text{ cm}^{-3}$ .

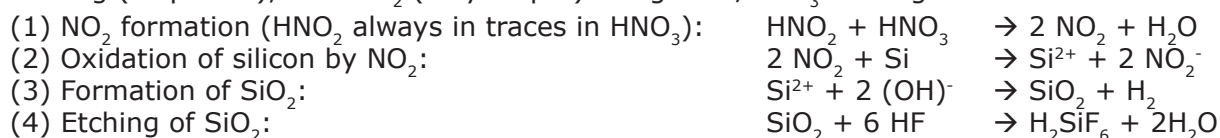
The following table lists etch rates of Si and the hard masks  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$ , and etch selectivity between different crystal planes as a function of the etchant.



## Isotropic Etching of Silicon and SiO<sub>2</sub>

| Etchant                    | Etch rate ratio |             | Etch rate (absolute) |                                |                  | Advantages (+)<br>Disadvantages (-)                                            |
|----------------------------|-----------------|-------------|----------------------|--------------------------------|------------------|--------------------------------------------------------------------------------|
|                            | (100)/(111)     | (110)/(111) | (100)                | Si <sub>3</sub> N <sub>4</sub> | SiO <sub>2</sub> |                                                                                |
| <b>KOH</b><br>(44%, 85°C)  | <b>300</b>      | <b>600</b>  | 1.4 µm/min           | <1 Å/min                       | 14 Å/min         | (-) Metal ion containing<br>(+) Strongly anisotropic                           |
| <b>TMAH</b><br>(25%, 80°C) | <b>37</b>       | <b>68</b>   | 0.3-1 µm/min         | <1 Å/min                       | 2 Å/min          | (-) Weak anisotropy<br>(+) Metal ion free                                      |
| <b>EDP</b><br>(115°C)      | <b>20</b>       | <b>10</b>   | 1.25 µm/min          | 1 Å/min                        | 2 Å/min          | (-) Weak anisotropy, toxic<br>(+) Metal ion free, metallic hard masks possible |

The following chemical reactions summarize the basic etch mechanism for isotropic silicon etching (steps 1-4), and SiO<sub>2</sub> (only step 4) using a HF/HNO<sub>3</sub> etching mixture:



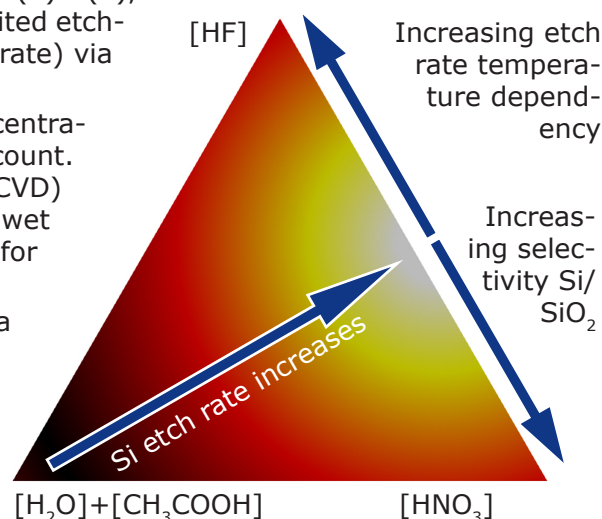
In conclusion, HNO<sub>3</sub> oxidises Si, and HF etches the SiO<sub>2</sub> hereby formed.

Fig. right-hand: High HF : HNO<sub>3</sub> ratios promote rate-limited etching (strong temperature dependency of the etch rate) of Si via the oxidation (1) - (3), while low HF : HNO<sub>3</sub> ratios promote diffusion-limited etching (lower temperature dependency of the etch rate) via step (4). HNO<sub>3</sub>-free HF etches do not attack Si.

The SiO<sub>2</sub> etch rate is determined by the HF-concentration, since the oxidation (1) - (3) does not account. Compared to thermal oxide, deposited (e. g. CVD) SiO<sub>2</sub> has a higher etch rate due to its porosity; wet oxide a slightly higher etch rate than dry oxide for the same reason.

An accurate control of the etch rate requires a temperature control within  $\pm 0.5^\circ\text{C}$ . Dilution with acidic acid improves wetting of the hydrophobic Si-surface and thus increases and homogenizes the etch rate.

Doped (n- and p-type) silicon as well as phosphorus-doped SiO<sub>2</sub> etches faster than undoped Si or SiO<sub>2</sub>.



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